Industrial Lubricant Oils

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1. Theme description

Lubricants are products used mainly in engines to reduce friction among mechanical bodies. Contrary to the majority of petroleum products which are identified through several parameters (the specs), lubricants are commonly identified only by their real performance, which can be tested only experimentally in specialized laboratories. The most important lubricants' spec is the Viscosity Index (VI), a measure of viscosity variation at different temperatures.

Lubricants are a blend of "base oils" and several additives. Base oils are generally produced from crude oils, but could also be produced by petrochemical feed-stocks (synthetic lubs). Additives are chemicals produced by few oil companies and some chemical company focused on this field as Lubrizol. The effective lubs performance strictly depends on the additives mixture. Additives and base oils are normally commercialized on the market, so the majority of companies buy and blend them. Lubricants, after used (exhaust oils), may be collected and reprocessed in order to obtain "second-hand" marketable products. Lubricants are among the most sophisticated and the most technology-intensive products of refining. Given the lower demand with respect to other petroleum products they are produced only in a limited number of refineries.

2. Mineral Base Oils [1]

The mineral base oils quality strictly depends on the crude origin, also if it can be partially modified through refinery processes. The base oils are a mixture of hydrocarbons, including alkanes (paraffins), alkenes (olefins), alicyclic (naphthenes), aromatics and some “mixed hydrocarbons” (where in one molecule are different groups of the above molecules). Regarding the base oils production, the aromatics have a negative impact to the viscosity index. They also worsen the base oils characteristics, meanly increasing the deposit formations and reducing the oxidation resistance.

Over hydrocarbons base oils contain the non-hydrocarbon molecules normally present into crude oil. The main non-hydrocarbon components are sulphur, nitrogen and oxygen. The sulphur heterocyclics are the most abundant of them.

The base oils feed-stock is the vacuum heavy gas-oil and the following units are a solvent extraction to separated aromatics and a deparaffinization to extract heavy paraffines (waxes).

The solvent treatment may be replaced by hydrogen process, e. g. HDC, perfectly integrated and already present in some refinery. This allows good yields and excellent quality bases, although starting from a traditionally unsuitable crude. Figure 1 shows an integrated scheme for production of base oils, either through solvent extraction or through HDC. The process usually ends with a hydrofinishing unit which improves colour, stability, etc. Blending and additivation are the final steps.

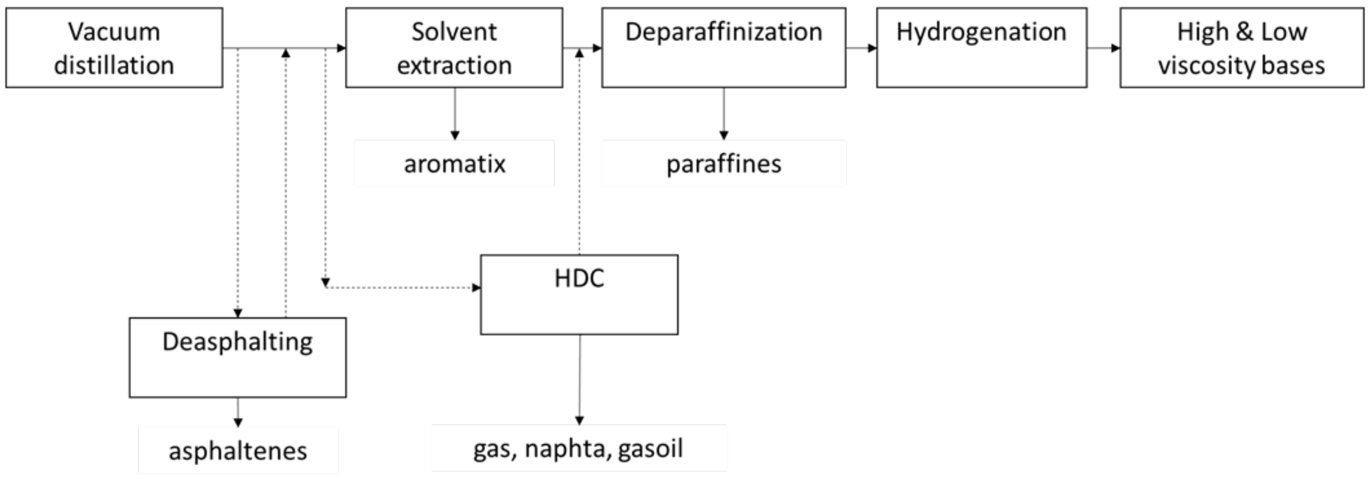

Figure 1 – Integrated cycle of base oil production in refinery (if hydrocracking process is available) [2]

Base oils cuts are internationally classified on the basis of viscosity SUS (Saybolt Universal Seconds) measured at 40 or 100 ° C (100 or 210 ° F). In addition, a code precedes the SUS viscosity value, such as, for example, SN (solvent neutral) or HVI (High Viscosity Index). The abbreviation BS (Bright Stock) is used for heavier cuts produced by the deasphalted residue. The crudes most suitable for base oil production are paraffinic ones, characterized by a high viscosity index (VI), but also by a high wax content. For certain applications, naphthenic crudes are more suitable because of the high-quality middle and low VI, the reduced content of wax and the naturally low sliding points.

Paraffinic base oils

Paraffinic base oils arising from paraffinic crudes are the most widely used.

The characteristics of these base oils depend on the original hydrocarbons composition, as well as on the effect of solvent extraction and de-waxing processes. The paraffinic base oils viscosity index is generally greater than 95 and the pour point is relatively high.

The viscosity index is as higher as stricter is aromatic extraction. It is also possible to increase the index by decreasing the de-waxing strictness but in this case there will be a worsening of the low temperature property.

Naphthenic base oils

Naphthenic base oils are produced from a few crudes (typically from Venezuela) and are currently used in a few applications where low-temperature properties are required and the viscosity index is less important.

These base oils have better solvent power, but low resistance to oxidation than paraffinic ones. Generally, they are also characterised by a low viscosity index (between 40 and 80) and a relatively low pour point due to the absence of paraffins.

3. Synthetic base oils

Most of the synthetic bases has both higher VI and flash points but lower pour points compared to mineral ones. On this basis, these oils are particularly useful in extreme temperature and pressure conditions.

The synthetic bases such as polyalphaolefins (PAO), alkylated aromatics, esters, polyglycols, polybutenes and polyinternalolefins (PIO) are widely used in lubricants industry.

Polyalphaolefin (PAO)

Polyalphaolefins show very good characteristics when operating at cold temperatures thanks to the high branching and volatility degree. However in some oxidation tests they appear less resistant than mineral bases (in absence of additives). This behaviour is due to the absence of natural antioxidants, present in the mineral oils. PAOs are less polar and thus they have low solvent power (solvency). This comes at the expense of ability to solubilise the polar additives present in the lubricating oil and the oxidation products (rubbers) formed during the exercise. The wide range of temperatures where PAO can work, together with the excellent chemical and physical characteristics, allows their use in various application areas.

Alkylated aromatics

The alkylbenzenes have lower characteristics if compared to PAOs but are used in refrigerant oils thanks to their excellent solubility and low pour point.

Polyglycols

Generally, they have high viscosity index which make them particularly suitable to obtain lubricating oils for the transmissions but they have a low oxidation resistance.

Polybutenes

Polybutenes are cut-resistant polymers and are used as Viscosity Index Improver (VII). They have higher volatility but lower resistance to oxidation and lower viscosity compared to PAOs and esters. In synthetic lubricants, polybutenes are usually combined with esters and PAOs and may affect the control of the lubricant viscosity, arising low deposit’s formation and thickening.

Synthetic esters

The most immediate effect of the ester group on lubricant properties is a lower volatility and an increased flash point. The esters influence other properties such as thermal stability, the solvent power, the lubricity, the biodegradability.

Poly internal olefins (PIO)

PIOs are characterized by high viscosity index, excellent rheological behaviour at low and high temperature, low volatility and good thermal-oxidative behaviour. They are employed as lubricants for internal combustion engines or industrial machineries.

4. Non conventional base oils

Non conventional base oils (NCBO) are produced from vacuum cuts treated through hydrogen-processes. The two main processes are hydrocracking and waxes hydro-isomerization. NCBOs offer two important advantages: hydrogen-processes can replace solvent extraction, reducing the dependence on crude origin and they ensure high quality base oils (better than conventional ones) due to a lower volatility, higher viscosity index, better temperature stability and lower sulphur content.

5. Re-refined base oils

The re-refined bases are produced by re-processing exhausted oils which cannot be lost in the environment but must by low collected into authorized centres from where they can be sent to controlled combustion plants or re-refined.

The re-refining processes, which consist on a treatment for removing volatile and insoluble components and additives, are able to produce lubricant bases with the same characteristics of mineral bases.

Re-refining yields allow to obtain for every 100 kg of exhausted oil about 60 kg of re-refined oil.

The treatment ends with a hydrogen treatment which eliminates or reduces the content of polynuclear aromatics (PNA), carcinogenic agents.

6. Base oil categories

Lubricating base oils are classified according to the physical characteristics and / or production process. The API (American Petroleum Institute) classifies base oils into five groups [3].

Group I – These oils are usually processed with solvents and they have a good degree of solvency, but they are most vulnerable to oxidation and thermal degradation compared to oils processed in different manner. The oils of Group I are used in almost all applications in the automotive and industrial field and are important for the formulation of lubricating greases.

Group II – Oils subjected to mild hydrocracking and catalytic de-waxing. They have high saturation levels, and good performance in terms of thermal and oxidation stability. These oils are used in a large range of automotive and industrial applications.

Group III – Typically subjected to severe hydrocracking, advanced catalytic de-waxing, and / or hydro-isomerization, they have high viscosity indexes and very good thermal and oxidation stability. They are used primarily in the automotive sector.

Group IV – Oils produced synthetically. The main characteristics relate to low pour points, high viscosity indexes, excellent thermal stability and excellent oxidation stability. These oils are used primarily in the automotive industry, such as high-quality motor oils and transmission oils.

Group V – This group includes base oils which are not present in other groups such as naphthenic, esters and polyglycols.

Group	Sulfur (w%)	Saturated (w%)	Viscosity Index	Main Production Methods
I	>0.03	<90	80-120	Solvent extraction,
II	≤0.03	≥90	80-120	Hydrocracking, Isomerization, Solvent extraction
III	≤0.03	≥90	≥120	Hydrocracking, Isomerization,
IV	Poly*alpha*olefins			Synthetics
V	All the others			Solvent extraction, Hydrogenation, Synthetics

Table 1 – API Classification of base oils and related production method [4]

7. Lubricants from renewable sources

The development of lubricants is traditionally based on mineral oils due to good technical properties and reasonable price of mineral oil. A disadvantage of mineral oil is its poor biodegradability which may cause environmental pollution.

Consequently, the research has evolved in the field of **synthetic esters** used as lubricants, exploiting renewable resources for the production of fatty acids.

In this way, the lubricants are sustainable and biodegradable. The physic-chemical properties of esters are able to cover the entire range of technical requirements for the industrial lubricant development, ensuring high performances.

Experimental studies performed on synthetic esters have been done on different types of formulations, meanly in lubricants based on saturated and unsaturated esters [5].

The oxidation stability of saturated ester bases is higher than the one of unsaturated esters. Particularly for rapeseed oil the oxidation stability of saturated esters can be compared to the one of mineral oil bases. Esters exhibit less friction than mineral oil.

8. New trends in lubricant technology

In many industrial applications the technological advancement is strongly linked to innovation in the field of lubricants. For this reason, important efforts are made in order to improve their quality. The objective is twofold: on one hand the duration increasing and the friction reduction; on the other, the reduction of environmental impact due to the use of fossil lubricants.

To meet these challenges researches in the use of **ionic liquids** as new generation of lubricants are ongoing.

These new systems show a significant improvement in wear and friction. Ionic liquids consist of large molecules, asymmetric organic cations and an inorganic anions. The large size induce widespread charges and reduced electrostatic forces among anion so much to rarely form a regular crystal structure and they may be liquid at room temperature. Ionic liquids have different properties that make them suitable as potential lubricants. Their low volatility, low flammability and thermal stability allows to safely absorb the increase in temperatures and pressures that occur when there is high friction [6].

Another significant advantage is the variety of usable anions and cations, they estimate at least one million of possible combinations, each one with its specific properties [7]. This means that ionic liquids can be made specifically for particular applications with high flexibility. For example the specific tasks may concern the absorption on a surface, a particular reaction, miscibility in a base oil etc.

For well-known lubrication systems, such as steel to steel, as well as for difficult lubricating systems such as steel to aluminium, ionic liquids have been shown to have better performance than available commercial lubricants. However ionic liquids are currently more expensive than conventional lubricants, so they may be limited to niche applications. For these reasons, actually ionic liquids are promising as lubricant additives, where it is possible a more widespread use.

Numerous nanoparticles used as additives were explored in recent years. The results are very encouraging and show an overall improvement in performance in terms of friction and wear even with concentrations less than 2% (weight). In particular, some particles as CuO, ZnO and ZrO_2 showed better performance when compared to the normal additives [8].

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[1] This brief review is inspired from "Encyclopaedia of Hydrocarbons" by ENI, Treccani 2005, Vol 2.

[2] The figure is taken from "Encyclopaedia of Hydrocarbons" by ENI, Treccani 2005, Vol 2.

[3] http://www.wolfoil.com/it_com/technico-commercial/pst/Module_1.aspx

[4] The table is taken from "Encyclopaedia of Hydrocarbons" by ENI, Treccani 2005, Vol 2.

[5] B. Krzan, J. Vizintin 2004 “Ester Based Lubricants Deriwed From Renewable Resources”, Tribology in industry, Volume 26, No. 1&2.

[6] Minami, I.; Kamimuram, H.; Mori, S. 2007 “*Thermo-Oxidative stability of ionic liquids as lubricating fluids*”. J. Synth. Lubr., 24, 135–147.

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[8] A. Hern, Battez, 2008, “*CuO, ZrO2 and ZnO nanoparticles as anti-wear additive in oil lubricants*”, Elsevier.